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# UPSC CGS Exam

Mains Chemistry Paper II

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**CHEMISTRY**  
**Paper – II**

Time Allowed : **Three Hours**

Maximum Marks : **200**

**Question Paper Specific Instructions**

*Please read each of the following instructions carefully before attempting questions :*

*There are **FIFTEEN** questions divided under **THREE** sections.*

*Candidate has to attempt **TEN** questions in all.*

*The **ONLY** question in Section **A** is **compulsory**. In Section **B**, **SIX** out of **NINE** questions are to be attempted. In Section **C**, **THREE** out of **FIVE** questions are to be attempted.*

*The number of marks carried by a question / part is indicated against it.*

*Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.*

*Unless otherwise mentioned, symbols and notations have their usual standard meanings.*

*Assume suitable data, if necessary, and indicate the same clearly.*

*Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly.*

*Any page or portion of the page left blank in the Question-cum-Answer Booklet must be clearly struck off.*

*Answers must be written in **ENGLISH** only.*

## Some useful fundamental constants and conversion factors

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\text{Rydberg constant} = 2.178 \times 10^{-18} \text{ J}$$

$$c = 2.998 \times 10^8 \text{ ms}^{-1}$$

$$k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$m_e = 9.109 \times 10^{-31} \text{ kg}$$

$$F = 96485 \text{ C mol}^{-1}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$\pi = 3.142$$

$$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$1 \text{ \AA} = 10^{-8} \text{ cm} = 10^{-10} \text{ m} = 0.1 \text{ nm} = 100 \text{ pm}$$

$$1 \text{ atm} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa}$$

$$1 \text{ bar} = 1 \times 10^5 \text{ Pa} = 0.9869 \text{ atm}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$1 \text{ L atm} = 101.34 \text{ J}$$

$$1 \text{ eV} = 23060 \text{ cal}$$

## SECTION A

**Q1. Answer all of the following questions :**

**5×16=80**

- (a) Explain the conditions under which real gases show the ideal behaviour. 5
- (b) Define compressibility factor ( $Z$ ). Describe  $Z$  vs.  $P$  plots with a suitable example. 5
- (c) A compound formed by elements  $X$  and  $Y$  crystallizes in the cubic structure.  $X$  atoms are situated at the corners and  $Y$  atoms are at the centre of faces. What is the formula of the compound ? 5
- (d) The data on the unit cell are given below. Identify the crystal system in each case. 5
- |       |                   |   |
|-------|-------------------|---|
| (i)   | $a = b \neq c$    | $\alpha = \beta = \gamma = 90^\circ$            |
| (ii)  | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90^\circ$            |
| (iii) | $a \neq b \neq c$ | $\alpha \neq \beta \neq \gamma \neq 90^\circ$   |
| (iv)  | $a = b \neq c$    | $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ |
| (v)   | $a = b = c$       | $\alpha = \beta = \gamma = 90^\circ$            |
- (e) Explain the electrophoretic effect in Debye-Hückel-Onsager theory of strong electrolytes. 5
- (f) Explain the terms : activity and activity coefficient. Write their units and magnitudes. 5
- (g) Why is a finely powdered substance a more effective adsorbent ? 5
- (h) Show that the half-life period of a first order reaction is independent of initial concentration of the reactant. 5
- (i) What is the role of phosphoric acid in the volumetric titration of  $\text{Fe}^{2+}$  ions and  $\text{Cr}_2\text{O}_7^{2-}$  ions when diphenylamine is used as internal indicator ? 5
- (j) Why can a voltmeter not be used for determining the EMF of a galvanic cell ? 5

- (k) What are well-behaved functions ? Which of the following functions are well-behaved ? 5
- (i)  $\phi(x) = e^{-\alpha x}$  ( $\alpha > 0$ )  $0 < x < \alpha$
- (ii)  $\phi(x) = \frac{1}{4-x}$   $1 < x < 10$
- (l) Suppose that the uncertainty in determining the position of an electron in an atom is  $0.4 \text{ \AA}$ . What will be the uncertainty in its velocity ? 5
- (m) Which of the following molecules are microwave active ? Why ? 5
- $C_2H_2$ ,  $CH_3Cl$ ,  $C_6H_6$ ,  $CO_2$
- (n) Which of the following molecules has the highest fundamental frequency of vibration ? Explain. 5
- $H_2$ ,  $D_2$ ,  $HD$
- (o) What are photosensitized reactions ? Explain with examples. 5
- (p) Calculate the energy in ergs, calories and electron volts in ultraviolet light of wavelength  $2500 \text{ \AA}$  absorbed per mole. 5

## SECTION B

Attempt any six questions :

10×6=60

**Q2.** What is the virial equation of state ? Derive the expression for the second virial coefficient from Van der Waals equation. 10

**Q3.** The first order reflections from the 100, 110 and 111 planes of a given cubic crystal were found to occur at angles  $5.9^\circ$ ,  $8.4^\circ$  and  $5.2^\circ$  respectively. Determine the type of crystal lattice to which the crystal belongs. 10

**Q4.** For a component in a homogeneous mixture, the chemical potential is given as

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

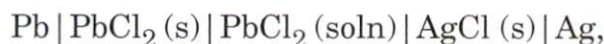
Show that  $\mu_i$  may be expressed in the following equivalent terms : 10

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} = \left( \frac{\partial A}{\partial n_i} \right)_{T, V, n_{j \neq i}} = \left( \frac{\partial H}{\partial n_i} \right)_{S, P, n_{j \neq i}} = \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}}$$

**Q5.** Outline the collision theory of bimolecular gaseous reactions. Show that it leads to the rate expression

$$r = P \left\{ \pi \sigma_{AB}^2 \left( \frac{8KT}{\pi \mu} \right)^{\frac{1}{2}} N_A^* N_B^* \right\} \exp \left( \frac{-E_0}{RT} \right).$$
 10

**Q6.** For the following cell



the potential at 298 K is 0.490 V and the variation of emf with temperature is given by

$$E = a - (1.86 \times 10^{-4} \text{ V/K}) (T - 25 \text{ K})$$

Calculate  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the reaction at 298 K. 10

- Q7.** What is the probability of locating a particle in one-dimensional box between  $\frac{L}{4}$  and  $\frac{3L}{4}$  where L is the length of the box ? Assume the particle to be in the lowest energy state. 10
- Q8.** (a) Sketch qualitatively the Raman spectrum showing Rayleigh, Stokes and anti-Stokes lines. Why are Stokes lines more intense than the anti-Stokes lines ? 7
- (b) State and illustrate the rule of mutual exclusion. Comment on the converse of this. 3
- Q9.** Describe the changes observed in the vibrational quantum number in an electronic transition using Franck-Condon principle. 10
- Q10.** (a) From the following reduction reactions and  $E^\circ$  values :
- $$\text{Fe}^{3+}(\text{aq}) + e \rightarrow \text{Fe}^{2+}(\text{aq}) \quad E_1^\circ = 0.772 \text{ V}$$
- $$\text{Fe}^{3+}(\text{aq}) + 3e \rightarrow \text{Fe}(\text{s}) \quad E_2^\circ = -0.036 \text{ V}$$
- Calculate  $E_3^\circ$  for the half-cell reaction
- $$\text{Fe}^{2+}(\text{aq}) + 2e \rightarrow \text{Fe}(\text{s}). \quad 5$$
- (b) Calculate the molecular diameter (d) of helium if its Van der Waals constant b is  $23.70 \text{ cm}^3 \text{ mol}^{-1}$ . 5

## SECTION C

Attempt any *three* questions :

20×3=60

- Q11.** (a) What is Boyle temperature ? Give its significance for the gases H<sub>2</sub>, He, N<sub>2</sub> and NH<sub>3</sub>. 10
- (b) Classify the solid state of the following substances as ionic / covalent / molecular / metallic crystals and explain. 5  
SiC, S<sub>4</sub>, KBr, LiCl, Mg
- (c) How does the temperature dependence of electrical conduction in an aqueous solution compare with that in metal ? 5
- Q12.** (a) Derive the Gibbs-Duhem equation in the term  $\sum_i n_i (d\bar{Y}_i) = 0$  at constant temperature and pressure where  $\bar{Y}_i$  is an extensive property of a solution. Describe the physical significance of the above equation. 10
- (b) For the first order reaction  
$$2\text{N}_2\text{O}_5 (\text{g}) \rightarrow 4\text{NO}_2 (\text{g}) + \text{O}_2 (\text{g})$$
  
A is  $4.3 \times 10^{13} \text{ s}^{-1}$  and K is  $4.329 \times 10^{-5} \text{ s}^{-1}$ , calculate the energy of activation at 300 K. 10
- Q13.** (a) How is the pH of a solution determined using hydrogen electrode ? 10
- (b) What are the steps involved in the mechanism of photochemical decomposition of hydrogen-iodide reaction ? 10
- Q14.** (a) What is degeneracy ? Illustrate with the cubic box of length L. How many eigenstates are there with energy equal to  $\frac{101 h^2}{8 mL^2}$  ? 10
- (b) Consider a particle moving in a three-dimensional box with sides a, b and c. Assuming  $n_1$ ,  $n_2$  and  $n_3$  as quantum numbers for the motions along x, y and z directions, write down the wavefunction and energy for this system. State whether the pair of Laplacian operator and this wavefunction satisfy the eigenvalue equation. If yes, what is the eigenvalue ? 10

- Q15.** (a) The  $J = 3 \rightarrow 4$  transition for a diatomic molecule occurs at  $0.50 \text{ cm}^{-1}$ . What is the wave number for the  $J = 6 \rightarrow 7$  transition for this molecule? Assume the molecule is a rigid rotor. 10
- (b) Sketch the fundamental vibration modes of  $\text{CS}_2$  and  $\text{OCS}$ . Which of these are IR active? 5
- (c) Why is a saturated solution of  $\text{KCl}$  or  $\text{NH}_4\text{NO}_3$  used in the salt bridge? 5

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